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PATENTS ACT, 1978
APPLICATION FOR A PATENT AND
ACKNOWLEDGEMENT OF RECEIPT
(Section 30(1) Regulation 22)

FORM P.1
(to be lodged in duplicate)

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THE GRANT OF A PATENT IS HEREBY REQUESTED BY THE UNDERMENTIONED APPLICANT ON THE BASIS OF THE PRESENT APPLICATION FILED IN DUPLICATE

PATENT APPLICATION NO.	
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71	FULL NAMES(S) OF APPLICANT(S)

A & A REF: 118904 AS/CST

ISO-STER [PROPRIETARY] LIMITED

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54 TITLE OF INVENTION

CROSS-LINKING OF POLYMERIC MATERIALS

Only the items marked with an "X" in the blocks below are applicable.

- [X] The Applicant claims priority as set out on the accompanying Form P.2
- [ ] The application is for a patent of addition to patent application no. |21|01|
- [ ] This application is a fresh application in terms of section 37 and based on Application No. |21|01|

THIS APPLICATION IS ACCOMPANIED BY:

- [X] ~~A single copy of a provisional or~~ two copies of a complete specification of . 22. .pages.
- [ ] Drawing of .. ... sheets.
- [X] Publication particulars and abstract (Form P.8 in duplicate) (for complete only).
- [ ] A copy of Figure......of the drawings (if any) for the abstract (for complete only).
- [X] An assignment of invention.
- [ ] Certified priority document(s) (State quantity):.........
- [ ] Translation of the priority document(s).
- [ ] An assignment of priority rights.
- [X] A copy of Form P.2 and the specification of RSA Patent Application No. |21|01| 88/5702
- [X] A Form P.2 in duplicate.
- [X] A declaration and power of attorney on Form P.3.
- [ ] Request for ante-dating on Form P.4.
- [ ] Request for classification on Form P.9.
- [ ] Request for delay of acceptance on Form P.4.
- [ ]

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DATED THIS 7TH DAY OF SEPTEMBER 1989

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A. & A. Ref. No. 118904 AS/CST

ADAMS & ADAMS
PATENT ATTORNEYS
BENSTRA BUILDING
PRETORIA

FORM P7

REPUBLIC OF SOUTH AFRICA
Patents Act, 1978

COMPLETE SPECIFICATION

(Section 30 (1) - Regulation 28)

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INTERNATIONAL CLASSIFICATION	
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TITLE OF INVENTION	
54	CROSS-LINKING OF POLYMERIC MATERIALS

THIS INVENTION relates to the production of artifacts comprising cured polymeric materials. More particularly the invention relates to a method of producing a cured polymeric artifact from a polymeric thermoplastic starting material, the material of the artifact having reduced thermoplasticity relative to the starting material and exhibiting an enhanced degree of cross-linking relative to the starting material; to a method of making a partially cross-linked polymeric thermoplastic material suitable for use as a feedstock for the production of polymeric artifacts and capable of being cured by heating to reduce its thermoplasticity; and to a method of making a master batch for use in the production of a cured polymeric artifact.

According to one aspect of the invention there is provided a method of producing a cured polymeric artifact from a polymeric thermoplastic starting material, the material of the artifact having reduced thermoplasticity relative to the starting material and exhibiting an enhanced degree of cross-linking relative to the starting material, the method including the steps of:

subjecting a polymeric thermoplastic starting material, which is capable of being cross-linked by irradiation, to sufficient irradiation partially to cross-link the starting material to produce a thermoplastic partially cross-linked intermediate material; and

reducing the thermoplasticity of the intermediate material by heating it to raise its melting point.

By raising the melting point of the intermediate material by heating is meant that, after such heating and subsequent cooling to ambient temperature, a product material will be obtained which has reduced thermoplasticity relative to the intermediate material in the sense that, when the product material is again heated, its melting point will be higher than the melting point of the intrmediate material.

The polymeric thermoplastic starting material may be based on any suitable polymeric thermoplastic base material, which may be a plastics, resinous or elastomeric [rubbery] material, and will typically contain a suitable proportion of a suitable cross-linking agent. Examples of base materials include homopolymers, co-polymers and ter-polymers of plastics material and rubbers which are thermoplastic, and blends thereof, eg polyethylene, polyvinyl chloride, segmented copolymers of butadiene and isoprene with styrene, natural rubber and polyethylene-ethylene propylene rubber blends. Accordingly, the starting material may comprise a mixture of a polymeric thermoplastic base material and a cross-linking agent, the base material being selected from the group consisting of:
polyethylene;
polyvinyl chloride;
segmented copolymers of butadiene and isoprene with styrene;
natural rubber;
blends of polyethylene, ethylene and propylene rubber; and
mixtures of the aforegoing,
the mixture being in the form of a continuous phase of the base material in which the cross-linking agent is a discontinuous phase dispersed in finely divided form.

The method may include the preliminary steps of compounding or formulating the starting material, by admixing with the polymeric base material or base materials a suitable cross-linking agent. Usually the cross-linking agent will comprise at least two chemically reactive unsaturated bonds such as double bonds in its molecule, some of which unsaturated bonds react with the base material during the partial cross-linking under the influence of the radiation to produce the intermediate material. Suitable cross-linking agents include multifunctional acrylates or methacrylates such as trimethylolpropane trimethacrylate [TRIM] and allyl derivatives such as triallyl cyanurate [TAC]; and the material may be compounded to contain 0,5-25% by mass of cross-linking agent. Compounding the material may take place in the usual way, eg by mixing the constituents to a sufficient

degree of homogeneity in the molten state at a temperature of typically not greater than 165°C and usually somewhat lower, and allowing the mixture to cool and set. Accordingly, in a particular embodiment, the method may include the preliminary step, before the irradiation, of compounding or formulating the starting material by admixing a cross-linking agent into a molten polymeric thermoplastic base material, the cross-linking agent comprising at least two unsaturated bonds in its molecule, which bonds are capable of reacting with the base material under the influence of the irradiation to cross-link the base material, the starting material being allowed to set before the irradiation is carried out.

The partial cross-linking may be effected by subjecting said material to ionising radiation, and may be effected at ambient temperature. Alpha, beta or gamma radiation may be employed, and can be produced by a suitable radioactive isotope such as cobalt 60 or a suitable electron beam accelerator which generates energetic electrons with an energy of eg 50 keV to 10 MeV. The absorbed radiation dose applied to said material during the partial cross-linking may be of the order of 4-100 kGy, and conventional electron beam machines or irradiators such as gamma irradiators can be employed for this purpose. In particular, the irradiation to which the starting material is subjected may be carried out at ambient temperature with the starting material in solid form by subjecting the starting material to sufficient radiation to apply an absorbed radiation dose to the starting material of 4-100 kGy.

The degree of cross-linking effected during the partial cross-linking by irradiation will be sufficient to provide an intermediate material which is thermoplastic; and the cross-linking effected by the irradiation may be sufficient to bind 10-50% by mass of the material, as determined by Soxhlet solvent extraction. The eventual properties of the cured material in turn depend on the temperature to which the intermediate is heated, the time spent at that temperature and the proportion of

cross-linking agent added, and heating will be for a period sufficient to provide the cured artifact product with the desired absence of or low level of thermoplasticity.

The method may include the step of subjecting the starting or intermediate material to a size reduction to render it particulate before the thermoplsticity of the intermediate material is reduced by heating.

In a particular embodiment of the invention, the method may include the steps of:

forming a master batch by admixing a cross-linking agent into a molten thermoplastic diluent polymeric material, the diluent polymeric material having a melting point at least 60°C less than that of the starting material;

subjecting the master batch to irradiation to cross-link the diluent polymeric material; and

admixing the master batch into a polymeric thermoplastic base material in molten form to form the starting material. The master batch may be allowed to cool and set before it is admixed into the base material; and the master batch may be subjected to a size reduction which renders it particulate before it is admixed to the base material.

As indicated above, in preferred embodiments of the invention, the cross-linking agent may be a member of the group consisting in multifunctional acrylates and methacrylates, multifunctional allyl derivatives and mixtures thereof; and the cross-linking by irradiation may be by ionizing radiation selected from alpha radiation, beta radiation, gamma radiation and mixtures thereof.

The heating may be to a temperature of 160-220°C for a period of 5-200 seconds, preferably to a temperature of 160-220°C for a period of 30-120 seconds. Generally the heating time will be inversely related to the temperature, a desired reduction in thermoplasticity being achieved more rapidly the higher the

temperature, bearing in mind constraints imposed by, on the one hand, the fact that too high a temperature can have adverse effects on the product material, and, on the other hand, too low a temperature can lead to unacceptably long cycle times. Generally routine experimentation will be employed to determine an acceptable or optimum temperature/time combination, bearing in mind practical and economic considerations.

The nature of the base polymer and the cross-linking agent and the proportion of cross-linking agent, the degree of partial cross-linking by radiation, the temperature of heating and the duration of such heating, etc, will be selected so that these parameters produce a product with the desired physical and chemical properties. As at least a rough guide, known base polymer/cross-linking agent formulations can be employed which, when fully cured by radiation, provide a product with desired physical and chemical properties.

The method may include, in addition to mixing the cross-linking agent into the base polymer, admixing one or more additives therein. Such additives include:

antioxidants [stabilizers] such as hindered phenol octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate;

ultra-violet radiation stabilizers such as poly-([6-[(1,1,3,3-tetramethyl butyl)-imino]-1,3,5-triazine-2,4-diyl][2-(2,2,6,6-tetramethyl piperidyl)-imino]-hexamethylene-[4-(2,2,6,6-tetramethyl piperidyl)-imino]);

plasticizers such as phthalic esters or epoxidized soya oil;

impact modifiers such as ethylene-vinyl acetate copolymer or nitrile rubber;

slipping agents such as oleamide;

fillers such as calcium carbonate;

reinforcers such as carbon black;

flame retardants such as antimony trioxide and organobromine;

coupling agents such as silanes;

fungicides such as phosphites;

anti-blocking agents such as amide waxes;
pigments such as rutile;
essences such as dimethyl phenyl carbonyl;
lubricants such as stearic acid or calcium stearate;
blowing agents such as azodicarbonamide; and/or
electronic conductors such as carbon black.

The additives used and the proportions thereof used will be similar to those employed for similar purposes in polymeric materials which are usually fully cross-linked and cured by irradiation.

An important feature of the invention arises from the fact that polymeric materials of the type in question are frequently employed by the conversion thereof in a fluid or a least mouldable state at an elevated temperature, eg by extrusion, injection moulding, blow moulding, casting or the like, into numerous different artifacts or articles of commerce such as pipes, bottle crates etc. During fabrication of such artifacts by conversion, a starting material, which is thermoplastic and is typically in powder, granule or chip form, is formulated or bought by the manufacturer of the artifact or article, and is converted at an elevated temperature, after which the article or artifact is caused or allowed to set. The artifact may thus be formed from a batch of material which has been heated to render it flowable, the forming being by moulding, casting or extruding after which the artifact is allowed to set, the heating to reduce the thermoplasticity of the intermediate material taking place no earlier than the forming.

Accordingly, the forming and the heating to reduce the thermoplasticity may take place simultaneously, the heating which acts to render the batch flowable also acting to effect the reduction in thermoplasticity. In other words, the heating of the intermediate material in terms of the method of the present invention may be carried out during such forming or conversion, eg during blow-moulding, injection-moulding, extruding, casting, etc of the intermediate. Thus, the temperatures employed for the

forming or conversion have been found to be suitable for, or can be selected to be suitable for, the heating step of the method of the present invention, and can be held during conversion for a period sufficient to effect the reduction in thermoplasticity. It follows that the composition of the starting material which is irradiated to provide the partial cross-linking, and the degree of cross-linking effected by radiation, are conveniently selected to provide an intermediate material which is suitable as a feedstock for a forming or conversion process of the type in question. In particular, the method of the present invention may be carried out to provide an intermediate material which is suitable for use as a feedstock in conventional forming or conversion machinery in conventional conversion processes.

It follows that, after or conveniently before the irradiation but after any compounding or formulation to provide the starting material from a cross-linking agent and polymeric thermoplastic base material, the material being processed in accordance with the method of the present invention may be subjected to the abovementioned size reduction, so as to produce the intermediate material in powder, granule or chip form, suitable as a feedstock for subsequent forming or conversion processes.

The invention also extends to a cured polymeric artifact whenever produced by the method described above.

According to another aspect of the invention there is provided a method of making a partially cross-linked polymeric thermoplastic material suitable for use as a feedstock for the production of polymeric artifacts and capable of having its thermoplasticity reduced by heating, the method including the step of subjecting a polymeric thermoplastic starting material, which is capable of being cross-linked by irradiation, to sufficient irradiation partially to cross-link the starting material.

The polymeric material which is irradiated may be formulated and irradiated as described above, and, after or conveniently before irradiation, may be converted into particulate material as described above, to produce an intermediate material which can be employed as a feedstock for a variety of conversion processes, which conversion may indeed take place after elapse of a considerable period and at a different location.

As mentioned above, the method of producing a cured polymeric artifact according to the present invention can involve the use of a master batch. This master batch can, naturally, be compounded or formulated in one location and then can be transported or stored for use in another location, during the forming or conversion of a polymeric thermoplastic base material into a polymeric artifact.

Accordingly, a further aspect of the invention provides a method of making a master batch for use in a method of producing a cured polymeric artifact from a polymeric thermoplastics starting material as described above, the method of making the master batch comprising the steps of:

admixing a cross-linking agent into a molten thermoplastic polymeric base material having a melting point of at most 180°C; and

thereafter subjecting the mixture to irradiation to cross-link the polymeric material.

As indicated above, the polymeric base material for the master batch may be selected from the group consisting of:
polyethylene;
polyvinyl chloride;
segmented copolymers of butadiene and isoprene with styrene;
natural rubber;
blends of polyethylene, ethylene and propylene rubber; and
mixtures of the aforegoing,

the mixture being in the form of a continuous phase of the polymeric base material in which the cross-linking agent is a discontinuous phase dispersed in finely divided form.

The mixture may be allowed to cool and set before it is irradiated; and the mixture may be allowed to cool and set before then being subjected to size reduction which renders it particulate. As indicated above, the cross-linking by irradiation may be by ionizing radiation selected from alpha radiation, beta radiation, gamma radiation and mixtures thereof, and is sufficient to apply an absorbed radiation dose to the polymeric material of 4 - 100 kGy; and the cross-linking by irradiation may be sufficient to bind 10 - 50 % by mass of the polymeric material. As described above, the cross-linking agent may comprise at least two unsaturated bonds in its molecule, being a member of the group consisting of multifunctional acrylates and methacrylates, multifunctional allyl derivatives, and mixtures thereof. More particularly, formulation or compounding of the master batch may be as described in more detail above with reference to the method of producing a cured polymeric artifact, and it should be noted that the polymeric base material used for the master batch will typically have a melting point substantially lower than that of the polymeric base material for the artifact into which it is eventually intended to be blended, the polymeric base material of the master batch typically having a melting point of less than 165°C, eg 150°C or less. The invention contemplates that the master batch material, after cooling and solidification, will be milled into powder, granules or chips for transport or storage before required for use when it can be mixed into the base material employed for the artifacts in molten form, for use for forming or conversion into an artifact at which stage the heating is provided to reduce the thermoplasticity. Naturally, after it is mixed into the bulk of the base material for the artifact, it can, without heating sufficiently to reduce its theremoplasticity, again be cooled and milled and kept for use later, but usually conversion and heating to raise the melting point will take place immediately after the

to raise the melting point will take place immediately after the blending. The base material for the master batch will naturally also be chosen so that it is physically and chemically compatible with the base material used for the eventual artifact.

The invention accordingly extends also to a master batch whenever made according to the method described above.

The invention will now be described, by way of non-limiting illustrative example, with reference to the following worked Examples.

EXAMPLE 1

A base material comprising Alkathene type polyethylene of grade LM3060P obtained from AECI Chlor-Alkali and Plastics Limited, Johannesburg was compounded with 1,5% by mass of TAC by blending in molten form at 150°C to form a substantially homogeneous mixture, together with 3 parts by mass of antioxidant stabilizer for every 100 parts by mass of polyethylene. The stabilizer was a hindered phenolic antioxidant introduced by said supplier.

The blend was allowed to set, divided into chips and was subjected to an absorbed dose of 25 kGy gamma radiation in a commercial gamma irradiator to effect partial cross-linking.

The chips obtained were found to be thermoplastic and capable of having their thermoplasticitiy reduced by heating to 165°C for about 1 minute into a fully cured non-thermoplastic product material. The degree of partial cross-linking achieved by the irradiation was found by Soxhlet extraction to be about 15% by mass of that in the heated product; and the chips after irradiation were found to be suitable as a feedstock

for conversion into articles of commerce by conversion processes operating at 165°C.

EXAMPLE 2

Example 1 was repeated except that Corvic type S6617 grade LBH polyvinyl chloride obtained from PVC Compounders [Proprietary] Limited, Benoni, Transvaal was used instead of the polyethylene as the base material. The cross-linking agent was TRIM and 10 parts by mass of said cross-linking agent for every 100 parts of polyvinyl chloride was used. The antioxidant stabilizer used was 4 parts by mass of a zinc-free barium/cadmium mixture for every 100 parts of polyvinyl chloride.

A 50 kGy absorbed dose was employed. Additional additives which were employed in the compounding of the material for cross-linking were:

Constituent	parts by mass/ 100 parts by mass of polyvinyl chloride
di-iso-octyl-phthalate [plasticiser]	90
epoxidized soya oil [secondary plasticizer stabilizer/extender]	4
stearic acid [internal lubricant]	0,2
calcium stearate [external lubricant]	1
nitrile rubber [impact modifier]	25
carbon black [pigment]	0,5

A thermoplastic intermediate was again obtained. This intermediate had about 37% by mass cross-linking [by Soxhlet extraction] and was capable of having its thermoplasticity reduced by heating to 165°C for about 1 minute, to obtain a non-thermoplastic product. The intermediate was again suitable for use as a feedstock for conversion at 165°C to produce artifacts by suitable conversion processes.

The invention, particularly as described with reference to the Examples, provides in principle certain substantial potential advantages and advances in the art when compared with similar methods known to the Applicant, whereby similar formulations compounded from thermoplastic polymeric base materials and cross-linking agents, together with similar additives, are cured exclusively by irradiation.

An important such advantage is that the present invention overcomes the problem of said prior methods that size constraints are imposed on the artifact or article of commerce which can be made. In the prior process, the article eg a large extrusion such as an extruded large diameter pipe or a large moulding, such as a bottle crate, must be extruded or moulded before cross-linking by radiation, while the formulation which has been compounded is still thermoplastic, bearing in mind that full curing by radiation renders the material non-thermoplastic. If the article produced by the conversion is too large for the irradiator or electron beam machine in question, cross-linking, with its attendant advantages of superior physical and chemical properties for many applications, must be dispensed with. In other words, the size, physical dimensions and design [shape] of the article produced by the conversion are limited by the size and design of the irradiation facility [irradiator or electron beam machine], which effectively rules out irradiation of certain artifacts by means of small irradiators or electron beam machines.

In contrast, the Applicant has found that a variety of base materials, when compounded with suitable proportions of suitable accelerators or cross-linking agents of the type generally used for irradiation curing, are capable of initial partial cross-linking by irradiation, after which reduction in thermoplasticity can be taken further simply by heating. This is particularly surprising as the Applicant has found that none of the base materials which it has tested, after compounding

with cross-linking agents, is suitable for cross-linking, thereby to obtain reduced thermoplasticity, merely by heating. It appears that the initial partial cross-linking by irradiation can be regarded as unexpectedly providing a product whose thermoplasticity can be reduced, and whose melting point can be raised, merely by heating.

Importantly, sufficient cross-linking can be achieved by irradiation to make possible a reduction in thermoplasticity by sufficient subsequent heating, without unacceptable loss of the thermoplastic nature of the intermediate material so that, after irradiation, conventional conversion processes, which rely on the thermoplastic nature of their feedstock for utility, can be used on the intermediate material. Furthermore the temperatures at which such conventional conversion processes operate, and the periods for which the feedstock is held at such temperatures, have been found to be suitable for the reduction of thermoplasticity, which reduction in thermoplasticity can easily be effected by routine operation, without substantial modification, if any, of such conversion processes or machines.

The intermediate of the present invention thus constitutes a potentially valuable commercial feedstock, as it can be used to make products by conversion without limitation caused by the irradiation facility as to size, physical dimensions, design or shape of the product. Large pipes can be extruded, eg up to 1000 mm diameter or more, and large mouldings of complex shape such as bottle crates, can be moulded by blow moulding or extrusion moulding. The size of the product is limited only by what the conversion process can make, and not by what the irradiator or electron beam machine can handle.

The Applicant thus contemplates compounding suitable materials for irradiation, converting them into chip or other suitable particulate form, and conveying them continuously in chip form, eg on a suitable conveyor at high production rates through an irradiator or electron beam machine which can be of

relatively small size. The partially cross-linked thermoplastic intermediate of the invention thus lends itself to efficient mass production using an irradiator or electron beam machine of any size; and can then be used or sold to users as a feedstock which can be used on conversion machines and in conversion processes requiring little if any modification to handle it.

Particular applications of the invention are in the manufacture of pipes of a diameter too great to be handled by presently available irradiations or electron beam machines; and the manufacture of articles such as bottle crates which are subject to theft by persons who render them into chips as feedstock for other conversion processes if they are of sufficiently thermoplastic material. When made by the present method, such crates or the like can be of a cross-linked material which is sufficiently non-thermoplastic to be unsuitable as feedstock, and will not be stolen for this purpose.

CLAIMS

1. A method of producing a cured polymeric artifact from a polymeric thermoplastic starting material, the material of the artifact having reduced thermoplasticity relative to the starting material and exhibiting an enhanced degree of cross-linking relative to the starting material, the method including the steps of:

subjecting a polymeric thermoplastic starting material, which is capable of being cross-linked by irradiation, to sufficient irradiation partially to cross-link the starting material to produce a thermoplastic partially cross-linked intermediate material; and

reducing the thermoplasticity of the intermediate material by heating it to raise its melting point.

2. A method as claimed in claim 1, in which the starting material comprises a mixture of a polymeric thermoplastic base material and a cross-linking agent, the base material being selected from the group consisting of:
polyethylene;
polyvinyl chloride;
segmented copolymers of butadiene and isoprene with styrene;
natural rubber;
blends of polyethylene, ethylene and propylene rubber; and
mixtures of the aforegoing,
the mixture being in the form of a continuous phase of the base material in which the cross-linking agent is a discontinuous phase dispersed in finely divided form.

3. A method as claimed in claim 1 or claim 2, which includes the preliminary step, before the irradiation, of compounding or formulating the starting material by admixing a cross-linking agent into a molten polymeric thermoplastic base material, the

cross-linking agent comprising at least two unsaturated bonds in its molecule, which bonds are capable of reacting with the base material under the influence of the irradiation to cross-link the base material, the starting material being allowed to set before the irradiation is carried out.

4. A method as claimed in any one of the preceding claims, in which the irradiation to which the starting material is subjected is carried out at ambient temperature with the starting material in solid form by subjecting the starting material to sufficient radiation to apply an absorbed radiation dose to the starting material of 4-100 kGy.

5. A method as claimed in any one of the preceding claims, in which the cross-linking effected by the irradiation is sufficient to bind 10-50% by mass of the starting material, as determined by Soxhlet solvent extraction.

6. A method as claimed in any one of the preceding claims, which includes the step of subjecting the starting or intermediate material to a size reduction to render it particulate before the thermoplasticity of the intermediate material is reduced by heating.

7. A method as claimed in claim 1 or claim 2 , which includes the steps of:

forming a master batch by admixing a cross-linking agent into a molten thermoplastic diluent polymeric material, the diluent polymeric material having a melting point at least 60°C less than that of the starting material;

subjecting the master batch to irradiation to cross-link the diluent polymeric material; and

admixing the master batch into a polymeric thermoplastic base material in molten form to form the starting material.

8. A method as claimed in claim 7, in which the master batch is allowed to cool and set before it is admixed into the base material.

9. A method as claimed in claim 8, in which the master batch is subjected to a size reduction which renders it particulate before it is admixed into the base material.

10. A method as claimed in any one of the preceding claims, in which the cross-linking agent is a member of the group consisting of multifunctional acrylates and methacrylates, multifunctional allyl derivatives and mixtures thereof.

11. A method as claimed in any one of the preceding claims, in which the cross-linking by irradiation is by ionizing radiation selected from alpha-radiation, beta radiation, gamma radiation and mixtures thereof.

12. A method as claimed in any one of the preceding claims, in which the heating is to a temperature of 160 - 220°C for a period of 5 - 200 seconds.

13. A method as claimed in any one of the preceding claims, in which the artifact is formed from a batch of material which has been heated to render it flowable, the forming being by moulding, casting or extruding after which the artifact is allowed to set, the heating to reduce the thermoplasticity of the intermediate material taking place no earlier than the forming.

14. A method as claimed in claim 12, in which the forming and heating to reduce the thermoplasticity take place simultaneously, the heating which acts to render the batch flowable also acting to effect the reduction in theremoplasticity.

15. A method of producing a cured polymeric artifact from a polymeric thermoplastic starting material, the material of the artifact having reduced thermoplasticity relative to the starting material and exhibiting an enhanced degree of cross-linking relative to the starting material, the method being substantially as described herein.

16. A cured polymeric artifact whenever produced by the method of any one of the preceding claims.

17. A method of making a partially cross-linked polymeric thermoplastic material suitable for use as a feedstock for the production of polymeric artifacts and capable of having its thermoplasticity reduced by heating, the method including the step of subjecting a polymeric thermoplastic starting material, which is capable of being cross-linked by irradiation, to sufficient irradiation partially to cross-link the starting material.

18. A method as claimed in claim 17, in which the starting material comprises a mixture of a polymeric thermoplastic base material and a cross-linking agent, the base material being selected from the group consisting of:
polyethylene;
polyvinyl chloride;
segmented copolymers of butadiene and isoprene with styrene;
natural rubber;
blends of polyethylene, ethylene and propylene rubber; and
mixtures of the aforegoing,
the mixture being in the form of a continuous phase of the base material in which the cross-linking agent is a discontinuous phase dispersed in finely divided form.

19. A method as claimed in claim 17 or 18, which includes the preliminary step, before the irradiation, of compounding or formulating the starting matertial by dissolving a cross-linking agent in a molten polymeric thermoplastic base material, the

cross-linking agent comprising at least two unsaturated bonds in its molecule, which bonds are capable of reacting with the base material under the influence of the irradiation to cross-link the base material, the starting material being allowed to set before the irradiation is carried out.

20. A method as claimed in claim 18 or claim 19, in which the cross-linking agent is a member of the group consisting of multifunctional acrylates and methacrylates, multifunctional alkyl derivatives and mixtures thereof.

21. A method as claimed in any one of claims 17 to 20 inclusive, in which the irradiation to which the starting material is subjected is carried out at ambient temperature with the starting material in solid form by subjecting the starting material to sufficient ionizing radiation selected from the group consisting of alpha radiation, beta radiation, gamma radiation and mixtures thereof, to apply an absorbed radiation dose to the starting material of 4-100 kGy.

22. A method as claimed in any one of claims 17 to 21 inclusive, in which the cross-linking effected by the irradiation is sufficient to bind 10-50% by mass of the starting material, as determined by Soxhlet solvent extraction.

23. A method as claimed in any one of claims 17 to 22 inclusive, which includes the step of subjecting the starting material to a size reduction to render it particulate.

24. A method of making a partially cross-linked polymeric thermoplastic material suitable for use as a feedstock for the production of polymeric artifacts and capable of having its thermoplasticity reduced by heating, substantially as described herein.

25. A partially cross-linked polymeric thermoplastic material suitable for having its thermoplasticitiy reduced by heating,

whenever made according to the method of any one of claims 17 to 24 inclusive.

26. A method of making a master batch for use in a method as claimed in claim 7, the method comprising the steps of:

admixing a cross-linking agent into a molten thermoplastic polymeric base material having a melting point of at most 180°C; and

thereafter subjecting the mixture to irradiation to cross-link the polymeric material.

27. A method as claimed in claim 26, in which the polymeric base material is selected from the group consisting of:
polyethylene;
polyvinyl chloride;
segmented copolymers of butadiene and isoprene with styrene;
natural rubber;
blends of polyethylene, ethylene and propylene rubber; and
mixtures of the aforegoing,
the mixture being in the form of a continuous phase of the polymeric base material in which the cross-linking agent is a discontinuous phase dispersed in finely divided form.

28. A method as claimed in claim 26 in which the mixture is allowed to cool and set before it is irradiated.

29. A method as claimed in any one of claims 26 to 28 inclusive, in which the mixture is allowed to cool and set and is then subjected to size reduction which renders it particulate.

30. A method as claimed in any one of claims 26 to 29 inclusive, in which the cross-linking by irradiation is by ionizing radiation selected from alpha radiation, beta radiation, gamma radiation and mixtures thereof, and is sufficient to apply an absorbed radiation dose to the polymeric material of 4 -100 kGy.

31. A method as claimed in any one of claims 26 to 30 inclusive, in which the cross-linking by irradiation is sufficient to bind 10 - 50% by mass of the polymeric material.

32. A method as claimed in any one of claims 26 to 31 inclusive, in which the cross-linking agent comprises at least two unsaturated bonds in its molecule, and is a member of the group consisting of multifunctional acrylates and methacrylates, multifunctional alkyl derivatives, and mixtures thereof.

33. A method of making a master batch for use in a method as claimed in claim 7, substantially as described herein.

34. A master batch for use in a method as claimed in claim 7, whenever made according to the method of any one of claims 26 to 33 inclusive.

DATED THIS 7TH DAY OF SEPTEMBER 1989

ADAMS & ADAMS
APPLICANTS PATENT ATTORNEYS